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Second NATO Workshop on Passive Infrared  
Optical Materials and Coatings

Robert W. Schwartz

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## SECOND NATO WORKSHOP ON PASSIVE INFRARED OPTICAL MATERIALS AND COATINGS

### 1 INTRODUCTION

The Second NATO workshop on Passive Infrared Optical Materials and Coatings was held at the Royal Signals and Radar Establishment (RSRE), Great Malvern, England, 8 through 10 September 1986. The first workshop on this topics was held in 1980. The workshop was organized by Dr. J.A. Savage of RSRE. About 50 delegates from the US, UK, France, and Germany attended. Forty-two papers were presented in the four sessions. In addition to these presentations, suggestions were solicited, in writing, as to what areas require further investigation. A compilation of these should now be available from the sponsor, NATO AC/243 (Panel III RSG 2). This is an abridged version of the conference report. A more complete version will be issued as a Naval Weapons Center Technical Paper 6786. In this shortened version, details will only be given of European presentations.

### 2 NATIONAL OVERVIEWS

Only Great Britain and the USA presented overviews. The British program was reviewed by G. Simpson from the Directorate of Components, Valves [i.e., tubes] and Devices in the Ministry of Defense. He first reviewed past successes such as the development of commercial optical-grade germanium for use in IR optics, the production of ZnS via chemical vapor deposition (CVD), and the commercialization of diamondlike carbon coatings. The present program is entirely in research, with the aim of screening materials and identifying those that seem reasonable for specific applications. Since materials development is costly and time consuming, the decision has been made to use the same technology for all materials. The chosen technology is a combination of sintering to closed porosity, in a neutral or partially reactive atmosphere if necessary, followed by hot isostatic pressing (HIP). The success of this ap-

proach will depend very heavily on the production of high-quality powders of all materials to be processed.

The UK's Plessey Research is trying to prepare high-strength IR windows of  $ZrO_2 \cdot Y_2O_3$  via organometallic precursors. Unagglomerated, spheroidal particles  $\sim 0.3 \mu m$  have been made, but the direction of the work has moved towards a gel approach, mainly due to the difficulty in obtaining adequate and reliable yttrium organometallic precursors. A ceramic made from zircar 45-mole-percent  $Y_2O$  has shown a transmittance of 65 percent between 5 and 6  $\mu m$  and a single water drop impact threshold velocity of 750 m/s (3.8 mm drops).

British Drug House (BDH), Ltd., uses the evaporative decomposition of solution method to prepare fine-grained calcium lanthanum sulfide. A mixed nitrate solution is sprayed through a furnace at about 1000°C. A 7-hour operation yields 50 g of mixed oxide precursor powder which is fired at 950°C in  $H_2S/N_2$  for 24 hours.

### 3 BULK MATERIALS--WINDOWS

R. Gentilman (Raytheon Company, US) talked about the optical, durability, and cost trade-offs for current and emerging 3- to 5- $\mu m$  dome materials. He gave an excellent review of the optical and thermomechanical characteristics of  $MgF_2$ , sapphire, spinel, aluminum oxynitride,  $MgO$ , and yttria dome materials.

The French delegate, P. Braudeau (Desmarquest), spoke about the production of thick IR-transparent  $MgF_2$  parts by HIP. Demarquest has been producing  $MgF_2$  for 10 years by hot pressing. That technique is costly and poorly suited to the production of thick parts. To overcome these handicaps work was carried out to optimize the HIP of  $MgF_2$  powder. Dense crack-free  $MgF_2$  pieces with transmittance close to that of conventional hot pressed  $MgF_2$  were produced. The processing involved cold isopressing, prefiring, machining, encapsulating in mild steel containers, and HIP between 600 to 700°C and 100 to 200 MPa.

B. Duchart (Barr and Stroud, UK) spoke on the production of ZnS by chemical vapor deposition. Material is produced from elemental Zn and H<sub>2</sub>S between 500 to 800°C at pressures of 50 mbar. Scale-up has been achieved and pieces several meters square have been grown. A typical CVD run can produce several hundred kilograms worth of pieces. The ZnS exhibits columnar growth with columns being about five to ten times as long as they are wide. However, the columns are themselves polycrystalline along their length. Grain size is dependent on growth temperature. Fracture strength was found to increase significantly as the temperature was raised. Duchart believes that fracture initiates at a few very large grains. Duchart also discussed postgrowth HIP of CVD ZnS. The CVD material has a large absorption band at 6  $\mu\text{m}$  due, it is thought, to ZnH and a great deal of scatter in the visible and near-IR regions caused by the presence of growth defects and some material with the hexagonal structure. If the CVD material is heated to remove the hydride, scatter continues to be a problem. If the ZnS is treated by HIP, the impurity is removed and grain growth takes place. This treatment eliminates the growth defects and gives a preferential alignment of the grains along the  $\langle 111 \rangle$  direction. This results in clear, colorless ZnS showing no optical losses over the wavelength range of 0.4 to 12  $\mu\text{m}$ .

J. Lewis (Plessey Research) reported on the UK effort to develop CaLa<sub>2</sub>S<sub>4</sub> as a LWIR material. Work has concentrated on the optimization of the IR transmissivity of this material and the evaluation of relevant thermal and mechanical properties. High-purity powders (typical particle size 0.5 to 2  $\mu\text{m}$ ) have been prepared to BDH (see above). The sulfide powder is processed into fully densified discs by a technique involving the sintering (in H<sub>2</sub>S at 1200 to 1500°C) of cold compacts ( $\sim 38$  MPa), followed by hot isostatic pressing (1000 to 1200°C to complete the densification and eliminate pores which could act as scattering centers. Except where otherwise stated, the properties listed in Table 1 are for

near-stoichiometric ceramics. The results indicate that strong, high-transmittance windows can be made from CaLa<sub>2</sub>S<sub>4</sub>; however, the high thermal expansion coefficient and the low thermal conductivity suggest that susceptibility to thermal shock may limit the usefulness of this material in thermal environments. Materials have absorption coefficients at 10  $\mu\text{m}$  to 0.2 to 0.5  $\text{cm}^{-1}$ .

TABLE 1  
Properties for Near-Stoichiometric  
Ceramics

Property	Units	CaLa <sub>2</sub> S <sub>4</sub>	ZnS*
Absorption coefficient			
at 8 $\mu\text{m}$	$\text{cm}^{-1}$	<0.5	0.1
Refractive index			
at 8 $\mu\text{m}$	--	2.55	2.20
Rupture modulus	MPa	$\sim 80$	103
Young's modulus	GPa	$\sim 80$	75
Hardness (KHN <sub>50</sub> )	$\text{kg/mm}^2$	600	250
Fracture toughness			
(K <sub>IC</sub> )	$\text{MPa}\cdot\text{m}^{1/2}$	0.6	--
Poisson's ratio	--	0.25	0.27
Thermal expansion			
(20-250°C)	$^{\circ}\text{K}^{-1}$	$14 \times 10^{-6}$	$7.4 \times 10^{-6}$

\* "Raytran" ZnS.

+  $12 \times 10^{-6}$  for very La-rich samples (Ca/La = 3/97); these are also free from CaS phase separation, which can cause significant scattering losses in near-stoichiometric material.

#### 4 BULK MATERIALS--INTERNAL COMPONENTS

West Germany's M. Baumgartner (Wacker Chemitronic) spoke on the fabrication of large-area semi-insulating CaAs and its potential for optical applications. Semi-insulating GaAs is an excellent material for IR optical windows and lenses in the wavelength range of 1.6 to 14  $\mu\text{m}$ . The undoped type is grown out of pyrolytic boron nitride (pBN) crucibles using the liquid-encapsulated Czochralski (LEC) technique. Chromium doping is required if the GaAs melt is kept in quartz containers during either LEC growth or Bridgman growth. Then the reaction between the melt and the quartz leads to

the incorporation of Si donors, which have to be compensated by the addition of deep Cr acceptors. For large-area crystals, LEC growth is preferable to Bridgman growth. Liquid-encapsulated Czochralski GaAs crystals of 5 inches in diameter have been demonstrated already. Unless special techniques are applied, Bridgman growth is generally limited to diameters less than 3 inches. Since the energy of the compensating deep levels--and thus, the Fermi level--is close to midgap, the free carrier concentration is very low. The activation energy for thermal generation of free carriers is typically 0.75 eV, which means that even at 200°C the carrier concentration is still below  $10^{12} \text{ cm}^{-3}$ . Therefore, free carrier absorption is negligible.

Also from West Germany, H. Krolla (Schott Glaswerke) reported on improvements in the production of Schott's IRG 100 chalcogenide glass. Schott produces a chalcogenide glass with a composition of  $\text{G}_{28}\text{Sb}_{12}\text{Se}_{60}$  with a capacity of 400 to 500 kg/yr and sells it under the trademark IRG 100. The transmission has been improved by using high-purity raw materials and by the addition of Ca and Sr as oxide getters. These are added at less than one weight percent and form small particles of  $\text{CaO}$  or  $\text{SrO}$ . These particles cause some scatter but have considerably reduced the deteriorating absorption band of  $\text{GeO}_2$ . The observed absorption coefficient at 10- $\mu\text{m}$  wavelength has a value of less than  $0.04 \text{ cm}^{-1}$ . The homogeneity within a set of samples from one melt has been improved so that the variation in the refractive index is guaranteed to be less than  $1 \times 10^{-4}$ . In actual measurements on plane discs of 100 mm in diameter and 10 mm in thickness, values for  $\Delta n$  of  $3 \times 10^{-5}$  were observed. The latter value is better than values measured for Ge ( $4 \times 10^{-5}$  to  $2 \times 10^{-4}$ ). The variation of the refractive index for samples from different melts is now less than  $2 \times 10^{-3}$ .

M.G. Scott (STC Technology Ltd., UK) dealt with infrared-transmitting fibers. The limited transparency of silica above about 1.8  $\mu\text{m}$  currently restricts the application of fiber optics to wavelengths in the visible and near-infrared. Halide

glass fibers, notably those based on metal fluorides, can transmit with moderate losses from the visible to beyond 4  $\mu\text{m}$ . Already, losses of a few tens of dB/km are routinely obtained, and values of 1 dB/km in the low-loss window at 2.5  $\mu\text{m}$  have been measured on short lengths. The potential losses of these fibers are lower than those of silica, making them attractive for nonrepeating data links of several hundred to a thousand kilometers in length. For longer wavelengths the various chalcogenide glass fibers can provide moderate losses from the near-infrared to as far as 12  $\mu\text{m}$ . In particular, those based on tellurides and selenides cover the long-wavelength output band. The losses of such fibers are currently a few dB/m at 10.6  $\mu\text{m}$ , making them suitable for short distance applications. Increased capability is promised by a new type of fiber based on a hollow core and a glass cladding. Losses of a few dB/m at 10.6  $\mu\text{m}$  have been demonstrated in silica clad fibers and the use of optimized materials is expected to reduce this value significantly. However, the bending losses of such fibers may restrict their use to situations where only moderate radii are experienced.

C. Le Sergeant (Laboratoires de Marcoussis, Research Center C.G.E., France) also spoke about chalcogenide fibers. Telluride-based chalcogenide glass fibers with improved optical, mechanical, and thermal properties have been achieved. These fibers have been manufactured by using a plastic-glass multiple co-drawing technique. Recently, progress has been made in producing Ge-As-Se-Te core and PFA-polyolefin-clad fibers, as well as some chalcogenide-clad fibers. Lengths up to a few hundred meters, with 400- $\mu\text{m}$  outer diameter and 200- $\mu\text{m}$  core diameter can be drawn, under inert gas. Loss lower than 1 dB/m in the range 5.5 to 10  $\mu\text{m}$ , and between 2 and 3 dB/m at 10.6  $\mu\text{m}$  (due to multiphonon absorption) has been measured at room temperature on  $\text{As}_{13}\text{Ge}_{25}\text{Se}_{27}\text{Te}_{35}$  core and PFA-polyolefin clad fibers. The minimal bending radius these fibers can afford is about 1 cm. These fibers may be used in the range from -50°C to +170°C. The loss increase

which is observed at high temperature is reversible. The mechanisms responsible for temperature sensitivity are not quite clarified.

## 5 BULK MATERIALS CHARACTERIZATION

P. Kuttner (Optische Werke G. Rodenstock, West Germany) presented information on measuring the homogeneity and birefringence of optical materials in the infrared spectral region. An instrument was constructed to make measurements in the 3- to 5- and 8- to 12- $\mu\text{m}$  regions. A refractive index gradient  $\Delta n/\Delta x$  in the radial direction of a disc of thickness "d" causes a deviation,  $\alpha$ , of a normal incident ray given by  $\alpha = d \Delta n/\Delta x$  and thus a lateral shift  $\Delta \epsilon$  of a fine line image. A fixed measuring slit positioned in the side of the image line converts variations in the shift,  $\Delta \epsilon$ , into variation of the luminous flux,  $\Delta \theta$ , which passes through the slit. The difference in refractive index can be found by integrating over the image. With this method, refractive index variations in the IR can be detected with an accuracy of  $1 \times 10^{-5}$ . Data show that monocrystalline germanium is more homogeneous than polycrystalline. Good materials show homogeneities of about  $2 \times 10^{-5}$ , but also materials with values as large as  $1 \times 10^{-4}$  are in use. If a birefringent disc is rotated between two crossed polarizers about the axis of the incident beam, the intensity of the emergent radiation,  $I$ , is proportional to  $\sin^2 2\theta \sin^2 \pi d \Delta n/\lambda$ . Here,  $\Delta n$  is the birefringence,  $d$  the thickness of the disc, and  $\theta$  the angle of rotation. The birefringence,  $\Delta n$ , can be derived from the amplitude of this sinusoidal signal. This method allows birefringence to be measured to about  $1 \times 10^{-5}$ . For germanium discs birefringence in the outer regions up to  $1.7 \times 10^{-4}$  was detected. The central parts show negligible birefringence.

The UK's A. Harrison (British Aerospace--BAe) presented data on the optical characterization of BAe zinc sulfide as it relates to imaging applications. Diamond machining of BAe zinc sulfide to generate high-quality optical surfaces

has been carried out. Measurements of homogeneity, refractive index, refractive index variation with respect to temperature ( $dn/dT$ ), optical imaging quality of Modulation Transfer Function (M.T.F.), and bulk scatter were described. Diamond machining of BAe zinc sulfide to generate high-quality optical surfaces has been carried out. Emphasis was placed on the measurement of single-wavelength optical imaging quality (MTF) and scatter which occurs due to microirregularities in the material or from surface effects in diamond-machined or in optically polished ZnS. The  $dn/dT$  was measured to be  $5 \times 10^{-5}$  up to  $80^\circ\text{C}$ . This was smaller than the sample-to-sample variation. Two samples measured had refractive indexes of  $2.22 \pm 0.004$  and  $2.19 \pm 0.004$ , respectively. The total integrated scatter at 0.632 and 10.6  $\mu\text{m}$  in the forward direction was measured on a number of flat plates. Values between 1.6 and 5.5 percent were found.

A.H. Lettington (RSRE, UK) reported on diamond turning of infrared components. Machines for the production of flat surfaces are well established. Diamond turning lathes for curved surfaces, however, require a high capital investment. Lettington described the development of a low-cost production machine based on a Bryant Symons diamond turning lathe.

K. Grosskopf (Ziess, West Germany) presented results on the fracture analysis of polycrystalline and monocrystalline germanium windows. In comparison with other IR-transmitting materials with low absorption between 8 and 12  $\mu\text{m}$ , germanium is distinguished by a relatively high mechanical strength and a low thermal expansion coefficient. Small pre-existing cracks in a germanium window can slowly propagate under tensile stresses and, therefore, determine quantities like strength, failure probability, and lifetime. Ziess performed double ring fracture test with 20 samples each. The Weibull curves indicated roughly 10 percent higher fracture stress for monocrystalline compared to polycrystalline germanium. The characteristic strength,  $\sigma_0$ , of the monocrystalline material is

162 MPa at a load increase rate of 18 MPa s<sup>-1</sup>. The polycrystalline material has a  $\sigma_0 = 151$  MPa. Double torsion tests were also carried out. The crack velocity,  $v$ , as a function of the stress intensity factor,  $K_I$ , did not show any significant difference between the two grades. Crack propagation occurred at  $K_I$ -values between 14 and 28 N m<sup>-3/2</sup> with  $40 \leq n \leq 70$  for the crack propagation parameter,  $n$ , according to  $v = AK_I^n$  for both monocrystalline and the polycrystalline germanium.

D. Townsend (Cavendish Laboratory, UK) discussed the hardness,  $H$ , and the fracture toughness,  $K_{IC}$ , of chemical-vapor-deposited zinc sulfide as functions of the grain size. For small grain size material (<50  $\mu$ m), the hardness, determined by Vickers indentation, was found to increase with decreasing grain size in accord with the Petch mechanism--i.e.,  $H = H_0 + ad^{-1/2}$ , where  $a$  and  $H_0$  are constants and  $d$  is the grain diameter. A maximum hardness of about 4 GPa has been observed for a material with a 0.5- $\mu$ m grain diameter. In large grain-size material, hardness anisotropy within the grains causes significant experimental scatter in the hardness measurements because the plastic impression formed by the indenter (load 10 N and 100 N) is smaller than the grain diameter. The values of  $K_{IC}$  obtained using an indentation technique show that zinc sulfide with a mean grain size of 8  $\mu$ m has the largest  $K_{IC}$ .

R.J. Hand (Cavendish Laboratory) discussed the fracture toughness and strength of ZnS in the temperature range from room temperature up to about 850 K. The fracture toughness and tensile strengths were measured using the so-called Brazilian test geometry. The  $K_{IC}$  values were obtained by first inserting a flaw of chosen size and known geometry using a Vicker's indenter.  $K_{IC}$  was found to increase with increasing temperature. The tensile strength increased in the range up to 373 K but then decreased, reaching the room temperature value at about 770 K. It seems probable, in view of the fact that all the strength increase occurs between room temperature and 373 K, that the strength increase is

due to removal of water from the sample itself. Failure was always found to initiate on the surface. The compressive strength was measured by loading cylindrical samples between anvils until catastrophic failure occurred. The compressive strength decreased to a value of about 80 percent of the room temperature value at 770 K.

Also from Cavendish Laboratory, J.E. Field reported on water drop impact: theory, equipment, and residual strength curves. Taking as an example a 2-mm-diameter water drop impacting at 500 m s<sup>-1</sup>, the initial pressures exceed 1.25 GPa and last for about 0.12  $\mu$ s. Studies of this initial high-pressure regime, including high-speed photographic sequences, were presented.

Field said that it is experimentally much simpler to study liquid/solid collisions if the solid specimen is kept stationary and the liquid is projected against it. He discussed a technique that has been developed at Cambridge University which projects a high-velocity jet of liquid at a stationary target. The collision velocity can be varied in the range up to about 3000 m s<sup>-1</sup>. By careful design of the chamber from which the jets are produced it has been possible to produce coherent jets with a smooth, slightly curved front interface. Such jets closely simulate liquid drop impact, since they reproduce the all-important initial geometry in the contact region. Recently, an apparatus has been developed for producing a sequence of jets (1 every 2 s) at velocities up to about 300 m s<sup>-1</sup>. This allows multiple liquid impact experiments to be performed. Of particular interest is the "threshold" velocity below which there is no damage. Techniques were developed for assessing damage quantitatively and obtaining these threshold values. Disc specimens are impacted by jet (or drops) of known size and velocity, and the "residual" (i.e., post-impact) strength of the specimen recorded. There is an initial plateau where the specimen strength is unaffected by the impact. However, above a "threshold" velocity the impact stresses can extend the defects in the solid, and the



strength falls. Such curves are particularly useful with brittle solids since they allow the effect of changing material properties, surface preparation, and the role of protective coatings to be assessed, and provide valuable design data for the engineer. Multiple impacts at the same point do not seem to decrease the threshold value; rather they sharpen the drop-off from the plateau and better define the threshold. Some thresholds measured for selected materials are:  $\text{Si}_3\text{N}_4=600 \text{ m s}^{-1}$ , sapphire= $500 \text{ m s}^{-1}$ , and  $\text{ZnS}=150 \text{ m s}^{-1}$ . Sapphire fails catastrophically just above its threshold because it is not a very tough material.

Field also spoke on the effect on contact stresses of single- or double-layer hard coatings. The effect of thin, hard coatings on the stress field generated by a spherical indentation on a flat half-space was investigated using a finite element program. It was shown that thin, hard coatings can have a significant effect on the radial and circumferential stresses. Of particular interest is the reduction in the maximum (radial) tensile stresses, since this indicates that hard coatings can be used to protect brittle materials against elastic contact damage. The stress reduction increases with the Young's modulus and thickness of the coating. The reduction in the substrate stresses is, however, accompanied by an increase in the maximum tensile stresses in the coating itself. Hard carbon or diamond-like coatings are potentially of great interest since they combine high moduli (typically 10 times higher than most substrate brittle solids such as glasses, etc.) with reasonably high strength. One calculated result for a situation with  $E_c=10 E_s$  and  $d/a = 0.1$  (where  $E_c$  and  $E_s$  are the moduli of coat and substrate, respectively,  $d$  is the coating thickness, and  $a$  the radius of the contact area) showed the maximum tensile stress at the coated interface is only 1/40th of that of the contact surface of a uniform half-space of the substrate material. Recent experimental work on germanium coated with hard carbon layers has shown that layers of 1- to 3- $\mu\text{m}$  thickness can in-

crease the loads required for ring crack formation and impact damage by factors of two or three. Double-layer coatings, where each has different elastic properties, were also analyzed. Comparison of double-layer coatings with monolayer coatings shows that for a given total coating thickness the substrate stresses are more effectively reduced by a monolayer of the harder of the two materials used in the double layer. However, for the double-layer coatings, the surface stresses in the outer coating are lower than in the case of monolayer coatings, in particular for larger coating thicknesses. Added to this is the practical advantage that a multilayer system can be built up to relatively large thicknesses without delamination.

C.J.H. Wort (Plessey Research, UK) presented a report on an optical technique for the evaluation of threshold velocity for water droplet impact damage. The zinc sulfide samples are 6x10x25 mm in size, the 6x15-mm and 10x25-mm faces being optically polished. The hard coating, which is opaque in the visible but highly transmissive over the whole of the 3.5- to 14- $\mu\text{m}$  band, is deposited on the 10x15-mm face, and is impacted three times at each of three velocities using a separate impact site for each velocity. The damage is observed by illuminating the sample with a diffuse light source through the 6x25-mm faces. The transmitted light is collected by a "vidicon" camera and displayed on a monitor. The damage is seen as a depth dependent reduction in transmitted light intensity; by scanning through the depth of the damaged region a clear map of the damage can be constructed. The data are processed and graphs of intensity reduction against depth for various impact velocities are used to yield a threshold velocity of about  $135 \text{ m s}^{-1}$  for damage in uncoated ZnS (in good agreement with other published data). Hard-coated samples exhibited a very significant increase of threshold velocity over that of the uncoated ZnS.

N.S. Corney (RAE, Farnborough, UK) presented some recent observations on the rain erosion of zinc sulfide and A-R

coated zinc sulfide. The transmission at 10  $\mu\text{m}$  of these materials decays in an approximately linear fashion with increasing erosion exposure time, without a significant initiation period. This rate of decay is a convenient measure of rain erosion resistance. As the impact angle is decreased from 90°C, the rate decreases more rapidly than would be expected from a simple sinusoidal function of impact angle. The rain erosion resistance of nine antireflection coatings deposited on zinc sulfide materials has been studied. Again, the decay of transmission is approximately linear with increasing erosion exposure, and the rate of decay increases rapidly with increasing impact angle. The effectiveness of these coatings has been compared in terms of initial transmission at 10  $\mu\text{m}$ , which should be as high as possible. All of the coating materials examined so far have greater erosion rates (in some cases as much as a factor of two greater) than the uncoated substrates. This could be due to delamination or damage of the coating.

France's A.A. Deom (Office National d'Etudes et de Recherches Aéronautiques) outlined the results of a comprehensive study of erosion and optical damage of various infrared materials using a rotating arm. The optical damage was characterized by measuring the change of the MTF with increasing time of exposure to a simulated rainfield. An optical infrared setup was built, allowing infrared MTF measurements of 17-mm-diameter samples. The dependence of optical degradation on impact velocity is similar to that of the mass loss; i.e., after an incubation period, the optical degradation increases quickly. An optical incubation time can be defined corresponding to a 10-percent loss of optical contrast. This characteristic time is also inversely proportional to a high exponent power law of the velocity. This exponent depends on the material. The optical degradation is dependent on the spectral range. The degradation in the 8- to 12- $\mu\text{m}$  range is generally weaker than for shorter wavelengths, a fact which was foreseeable. At first there is only loss of trans-

mission, but when the damage becomes significant there is also degradation of the MTF. The influence of other parameters, like impingement angle and droplet diameter, was studied. Generally a sine-law dependence of the impingement angle can be derived. The influence is quite small compared to the velocity dependence. It causes variations by a factor  $\pm 2$  upon the characteristic time. A simultaneous analysis of mass loss and optical damage is interesting. For some materials the two damages are synchronous; for others the optical damage can occur sooner than the mass loss. In the first case the optical damage is due to a deterioration of the surface, in the second case to an in-depth structural modification.

## 6 HARD COATINGS

J.M. Mackowski (Université Claude Bernard, France) presented some work on superhard coating. Diamondlike carbon films for antireflective coatings were prepared on germanium substrates by reactive R.F. sputtering, R.F. glow discharge of hydrocarbon gas, carbon ion beam sources, and dual ion beam sputtering. Without special care all methods lead to films with an absorption coefficient close to 300  $\text{cm}^{-1}$  in the 8- to 12- $\mu\text{m}$  range and with a Knoop hardness (10-g load) from 1000 to 4000  $\text{kg.mm}^{-2}$  (typically 2000  $\text{kg.mm}^{-2}$ ). The best results are obtained for films produced at low power in the 100- to 250°C temperature range and showing a hydrogen content close to 50 atomic percent as measured by FTIR quantitative spectroscopy and calibrated by nuclear reactions with  $^{15}\text{N}^{++}$  ions. The optical properties and adhesion strength of the films are strongly dependent on the carbon/germanium interface as measured by HTEM cross-section experiments. Optimized coatings show sharp monolayer interface with no carbon compounds.

L. Traub (Optical Coatings Limited [OCLI], UK) also spoke on the production of hard carbon coatings. Films of hard, diamondlike carbon were formed by the decomposition of a hydrocarbon gas in an R.F. plasma. Substrates are mounted on

the cathode which develops a negative self-bias as a result of the different mobilities of ions and electrons in the plasma. To ensure good coating adhesion it is normal to pre-etch the substrate surface in an argon discharge prior to deposition. The optical and environmental properties of the carbon films formed at the cathode are dependent on both the bias voltage and the hydrocarbon gas pressure. Transmission electron microscopy and electron diffraction studies suggest that the coating consists of diamondlike carbon crystallites embedded in an amorphous polymerized hydrocarbon matrix. Such films have been manufactured by OCLI on a production basis for over 3 years. Under optimum conditions, highly durable films of refractive index approximately 2.15 may be routinely deposited on germanium surfaces to provide good anti-reflection properties in the 8- to 12- $\mu$ m waveband. Absorption losses of films optimized for thermal imaging environmental applications are around 4 percent at 10  $\mu$ m. When subjected to severe abrasion testing, hard carbon coatings exhibit minimal reduction in transmission, even after prolonged abrasion, whereas conventional thermally evaporated coatings degrade relatively rapidly under the same conditions. Furthermore, hard carbon is resistant to acid and salt fog corrosion to a greater extent than evaporated coatings.

P. Koidl (Fraunhofer-Institut für Angewandte Festkörperphysik, West Germany) presented work on plasma deposition and properties of hard carbon coatings. He studied the deposition process using mass spectroscopy, optical emission spectroscopy, and probe measurements. In addition, the structural, chemical, and physical properties of the resulting films were characterized. The films are very high in hydrogen. The impact energy of the film-forming hydrocarbon ions, as measured by the negative bias voltage, is the most important parameter which strongly influences the optical and mechanical properties of the films. The type of hydrocarbon feed gas, on the other hand, influences the deposition rate but not the structure and properties

of the hard a-C:H films. Applications of hard a-C:H films as single or multilayer antireflection coatings for Ge, Si, and GaAs optics have been realized. The films have a very large absorption coefficient and are stable up to 500°C in air.

## 7 ANTIREFLECTION COATINGS

B.C. Monahan (Barr and Stroud, UK) spoke about multiband coatings. Multiband and broadband antireflection coatings applicable to a number of common infrared substrate materials were described. For zinc sulfide, a coating exhibiting very low reflectance (0.8 percent) at the 1.06- $\mu$ m neodymium YAG laser line and (about 3 percent) over the thermal band (to 12  $\mu$ m) has been designed. A variant of this coating is also suitable for zinc selenide. Chalcogenide glass is commonly used as a correcting element in infrared systems, and a very broadband antireflection coating covering the range of 2 to 12  $\mu$ m has been developed for use on internal surfaces. For germanium, the most common of all infrared substrate materials, two different broadband antireflection coatings have been successfully developed. The first, for internal germanium surfaces, simulates an inhomogeneous (graded index) layer which can provide low reflection over a very broad waveband. This is achieved by using a number of discrete layers to approximate to the ideal graded refractive index profile. For an external germanium surface, the aim has been to produce a dual-band coating (3 to 5  $\mu$ m and 8 to 12  $\mu$ m) exhibiting the outstanding abrasion resistance and chemical inertness which are proven features of the single-layer diamondlike carbon antireflection coating which has become the standard 8- to 12- $\mu$ m coating for harsh environments. This aim has been achieved through the use of an innovative plasma-assisted chemical vapor deposition technique (PACVD). This new coating is the forerunner of a family of superdurable multilayer coatings which can be prepared through the use of PACVD.

In his second presentation (see above) L. Traub also spoke on multiband antireflection coatings for ZnS. The

availability of water-clear multispectral zinc sulfide has given rise to the need for antireflection coatings operating efficiently at widely separated wavelengths for both multiband and dual band applications. The design techniques and process considerations underlying the manufacture of a broadband coating operating in the 2- to 12- $\mu\text{m}$  range and also a dual-band coating antireflecting both visible wavelengths and the 8- to 12- $\mu\text{m}$  band were discussed. In both instances, use was made of the Herpin Equivalent Index concept in the synthesis of initial designs. In the case of the broadband coating, a step-down antireflection approach was adopted, with optimum quarter-wave layer refractive indexes being initially determined from an algorithm providing good broadband response over the prescribed waveband. The number of steps was equal to  $\lambda(\text{long wave})/\lambda(\text{short wave})$ . Indexes which cannot be obtained using a single material are synthesized from three-layer symmetrical combinations. The choice of coating materials is determined from both optical and environmental considerations. Coatings produced were useful up to 350 to 400°C.

A.D. Wilson (Barr and Stroud, UK) presented work on progress towards coatings resistant to laser damage.  $\text{CO}_2$  laser-damage thresholds (LDT's) of a wide range of coatings were presented, the mechanisms of laser-induced damage (LID) were reviewed, and methods for eliminating the causes of LID were discussed. The low LDT's of many commercial multilayer coatings reflect the use of absorbing film materials--e.g.,  $\text{Y}_2\text{O}_3$ , Ge, etc. Such coatings were designed for good optical performance and abrasion resistance but without consideration of LID. It is possible to eliminate the absorbing materials to produce higher LDT coatings but other performance areas may suffer. Hard external surface coatings such as diamondlike carbon (DLC) also have high absorptance and hence low  $\text{CO}_2$  LDT's: greatly improving DLC coatings does not seem possible since the absorption is due mainly to fundamental C-C stretches. Consequently new ultrahard materials should be examined; such work is under way. With

the "low absorption" thin film materials commonly used in the IR, a range of LDT's may be found--sequential deposition runs giving widely differing values. Materials in use include  $\text{ThF}_4$ , with a refractive index of 1.3 and ZnS with  $n=2.2$  or ZnSe,  $n=2.4$ . These materials can be combined in numerous layers of various thickness to get the desired antireflection coatings. Recent work has shown that water contamination can occur in porous films of ZnS (on Ge substrates) and significantly reduce  $\text{CO}_2$  LDT's. Deposition at high substrate temperatures eliminates the porosity and, hence, water contamination and gives LDT's limited by damage to the substrate rather than the film. Indeed, such films when deposited on CVD ZnS substrates are indistinguishable from the substrate--i.e., have very high LDT's. Other methods of obtaining high-quality films (e.g., ion-assisted deposition, molecular beam epitaxy) are also being studied and give high LDT films. Such studies are giving a better understanding of laser/thin-film interactions and are leading to methods of improving film LDT's. However, the roles of interface absorption, of the substrate on the quality of film growth, of film stoichiometry, and of the physical perfection of the bulk film (on the atomic scale) need to be elucidated before the ultimate limits of film performance can be defined. Studies are under way in many of these areas.

K.L. Lewis (RSRE, UK) presented work on the growth and characterization of coatings resistant to laser damage produced by molecular beam epitaxy (MBE) techniques. These techniques have been used to produce optical thin films with a high resistance to laser-induced damage at 10.6  $\mu\text{m}$ . Films so far examined include ZnS, ZnSe,  $\text{SiO}_x$ ,  $\text{BaF}_2$ , and  $\text{PbF}_2$ . Cross-sectional transmission electron micrographs demonstrate that the films have a polycrystalline columnar morphology with grain size dependent on deposition temperature and film material, but in the range 250 to 1000 Å for ZnSe. A characteristic feature of ultrahigh-vacuum-grown films so far examined is the complete absence of porosity. Interface

perfection is high, and the presence of interfaces has negligible effects on laser damage thresholds in the cases so far examined. Impurity content can be kept very low. It is known that water in the  $10^{-5}$  to  $10^{-7}$  atm range is too high a pressure to produce damage-resistant films. The MBE technique allows a high degree of control over the film deposition process, thus so providing a means of depositing both novel materials (especially coevaporated species) and novel structures. Stratified structures have been deposited to assess the feasibility of microstructure control in optical coatings, and the requisite conditions have been explored to prevent propagation of columnar grains. This can be done by depositing two materials with lattice mismatches of 10 percent or more. The disruption of the columnar growth increases the laser-damage threshold. Such structures provide a basis for graded index thin film designs with the potential of control of the distribution of electric field under laser irradiation.

## 8 CHARACTERIZATION OF COATINGS

G. Habermann (Steinheil-Lear Siegler AG, Germany) reported on environmental testing of AR-coatings on Ge-optics. A typical sequence of environmental test methods for coatings on optical compon-

ents made from germanium was described. The complete test sequence is:

- o Adherence test with a specified cellulose tape
- o Abrasion test where a specified eraser is rubbed over the surface
- o Humidity test of the sample in a special test chamber
- o Solubility in a solution of sodium chloride and water
- o Salt spray test (the test which often shows coating defects that remained hidden even during former tests)
- o Temperature test at high and low temperatures
- o Windscreen wiper test, which is only applicable to very hard coatings
- o Test of chemical attack with liquids such as muriatic acid or acetone
- o Abrasion test repeated after completion of test sequence, to show whether the coating has maintained its original hardness.

Since most environmental tests on coatings are destructive, there is the possibility of testing witness samples coated alongside the actual optics. There are disadvantages to this method. There are also differences if a test sequence is executed on one single sample or if every test is carried out on a new witness piece.

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